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Incorporation of Iron into ZSM-5

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Project Number CM-RWT-0811

Incorporation of Iron into ZSM-5

A Major Qualifying Project Report

Submitted to the Faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the

Degree of Bachelor of Science

in Chemical Engineering

by

Iesha A. Boyce

Date: April 21, 2008

Approved:

Prof. R. W. Thompson, Advisor

Abstract

The objective of this project was to prepare iron incorporated ZSM-5 zeolites from silica gel beads using the hydrothermal treatment. A process for synthesizing these zeolites was developed, and zeolite beads containing a significant amount of iron were prepared. Samples were analyzed using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). Recommendations for improvement of the process were discussed.

Acknowledgements

First and foremost, I would like to acknowledge my Lord and Savior Jesus Christ through which all things are possible. I would also like to thank Professor Robert W. Thompson for his guidance and graduate students Engin Ayturk and Bradford Carleen for their help taking SEM images and XRD analysis.

TABLE OF CONTENTS

Introduction

Organic compounds are compounds containing carbon and hydrogen, with the exception of carbides, carbonates and carbon oxides. Although these compounds have many significant uses and applications, there are serious potential health risks involved with human exposure, some of which include: damage to the central nervous system, liver disease, kidney failure, anemia, and certain cancers. There are current regulations in place by the Unites States Environmental Protection Agency (EPA) on deposition levels by industrial sources and guidelines as to what content levels are safe for drinking. Some regulated organic compounds include: acrylamide, benzene, chlorobenzene, dichloromethane, ethylbenzene, styrene, toluene, tricholorethane, and vinyl chloride.

Due to their large use in industry, many of the compounds are emitted as byproducts or in waste streams of various syntheses and manufacturing processes. Other sources of emissions are the use of products manufactured or synthesized using these compounds. A major source of groundwater contamination is the storage of these hazardous wastes in tanks which are placed either in landfills or underground [1]. These tanks are then prone to leakage, and contaminants are released into the surrounding soil and, in turn, transferred to groundwater supplies. Groundwater is also contaminated due to effluent from water treatment facilities. Once the organic compounds are removed from the water, if they are not processed properly, they have the potential to cause contamination in groundwater supplies. Another major source is the discarding of household products containing these compounds such as: paints, aerosols, perfumes, and pharmaceuticals and personal care products (PPCPs).

Due to the high solubility and miscibility of some organic compounds in water, remediation of water sources used for drinking and other human uses is difficult. As a result, there are not many treatment options and the EPA is limited to the regulation of emissions, rather than treatment options. However, in most cases, for volatile organic compounds especially, treatment frequently consists of granular activated charcoal adsorption, packed tower aeration, and biodegradation. A more recent remediation strategy is advanced oxidation chemistry

The purpose of the project is to prepare spherical zeolites that are ¼ to ½ centimeter in size. At this size zeolites reduce pressure drops during extractions and, after being used to extract organic compounds, the zeolites have the potential to be cleansed of the waste and be reused. Zeolites are composed of mostly of silicon or aluminum bonded to oxygen causing a crystal lattice network to be formed. The cavities in these structures are ideal for the molecular sieving of organic compounds. This project will also consist of making zeolites in which iron is substituted for aluminum. Due to the catalytic capacity of iron, these zeolites may be used to mineralize organic compounds extracted from water.

Background

Overview

This study focused on the synthesis of beads of the high-silica zeolite, ZSM-5; with iron replacing aluminum in the zeolite's lattice structure. High-silica zeolites were synthesized for the extraction of organic compounds from water streams, with iron present as a catalyst. Background research on the description, uses, and synthesis of high-silica zeolites, specifically ZSM-5, was conducted, as well as research on iron catalyzed oxidation chemistry and the use of iron for the regeneration, or pore cleaning, of zeolites.

Applications of Zeolties

Zeolites are minerals with micro-porous structures. They are hydrated alumino-silicates that have cavities in their structures that are ideal for the accommodation of organic compounds. Compensating cations are loosely held by the structure, making these minerals ideal for ion exchange. Zeolites are also capable of molecular sieving, due to the uniformity in size of the cavities in a given zeolite. Over 150 types of zeolites have been synthesized, and over 48 naturally occurring types are known [2]. Naturally occurring zeolites are produced when alkaline groundwater reacts with volcanic rocks and ash layers. Another method by which naturally occurring zeolites were formed is crystallization, which occurred over periods of thousands to millions of years in shallow marine basins. Zeolites that occur naturally are contaminated to varying levels with other materials such as: metals, quartz, minerals, and other zeolites. Due to their impurities, they are oftentimes not included in commercial applications, in which uniformity and purity are essential for materials.

Uses

Although there is not much commercial use for naturally occurring zeolites, synthetic zeolites are widely used in many industries. Zeolites are used in ion exchange beds for the water purification process as well as the water softening process. Zeolites are used in chemistry as traps to separate molecules for analyzing. Zeolites also show potential to be used to separate water, carbon dioxide, and sulfur dioxide from natural gas streams [2].

In the petrochemical industry, zeolites are used as catalysts for processes such as fluid catalytic cracking and hydro-cracking, which take place in the internal cavities of the zeolites. Zeolites are ideal for reactions catalyzed by acidic sites occupied by protons, in which case it would be the compensating cation in the cavities of the zeolites. These hydrogen ion embedded zeolites are prepared by ion exchange and are powerful solid-state acids. They are capable of the facilitation of other reactions as well, such as isomerization and alkylation.

The shape selectivity of zeolites is the basis for their use for adsorption. Due to their ability to preferentially adsorb certain molecules, there is a vast range of molecular sieving applications. One application is the purification of para-xylene by silicalite. Unique from other isomers, para-xylene's shape, with two methyl groups on either end of the aromatic ring, allows is to diffuse rapidly through the zeolite, leaving ortho-xylene and meta-xylene isomers, whose structures consist of methyl groups that are closer together and act as obstructions, behind. This property can also be applied to the nuclear industry for reprocessing. In addition to the molecular sieving properties, the alumino-silicate structure of zeolites is extremely durable and resistant to radiation, even in the porous forms [2]. Once saturated with trapped fission products, the combination can be hot pressed into a durable, ceramic form with closed pores and waste trapped in a solid block. In addition to efficiency, producing this form of waste greatly reduces

the potential hazard as compared to conventional waste processing methods. Zeolites that contain cations can also effectively be used as desiccants, given that they have a high affinity for water. They can also be used for gas separation due to their electrostatic interactions with metal ions. One example of this application is the production of medical grade oxygen. In contrast to positively charged zeolites, non-polar zeolites can be used to adsorb organic solvents on the basis of size, shape, and polarity. Non-polar zeolites are synthesized by the dealumination of polar zeolites. Aluminum is removed by hydrothermal treatment at steam temperatures greater than 500 ˚C, which breaks the aluminum-oxygen bonds and thereby expels aluminum from the framework of the zeolite. Kneller et al. reported that mesopores and amorphous regions form upon dealumination, which may be a disadvantage [3]. The most common of these is the dealuminated Y (DAY) zeolite [2].

Zeolites have high heats of adsorption and remain chemically stable, while hydrating and dehydrating, which allows them to be used for heating and refrigeration. These properties make natural zeolites ideal for the storage of solar and waste heat energy. They are also used in construction in the process of warm mix asphalt. Zeolites assist in lowering the temperature in the manufacture and laying of asphalt, which reduces the use of energy needed for the process [4]. This, in turn, reduces the needed quantity of fossil fuels in the process, which has reduced emissions as a final outcome of their use. Also an asset to environmental improvement is the use of zeolites in laundry detergents. In powdered detergents, zeolites are used as a replacement for harmful phosphate builders, which served as powerful stain removers, which have been banned in many countries due to the water pollution risk associated with their use [2].

Removal of Organics from Water

Methyl tertiary butyl ether (MTBE) is a polar organic compound that is commonly used as a gasoline additive. MTBE and the spills and leaks associated with its use have resulted in serious environmental problems, which are primarily due to its high solubility in water. Standard remediation technologies have involved advanced oxidation, stripping, and sorption on granulated activated carbons (GAC). Recent studies have shown that high silica zeolites are an effective source of MTBE removal from water. Erdem-Şenatalar, et al. [5] found that high silica zeolites surpassed GAC in MTBE removal. Out of the four samples that were tested in the given study, Silicate-1, which had the highest silica to alumina ratio, proved to be the most efficient at removing MTBE at lower concentrations on the order of µg/L to mg/L. In contrast, DAY, which was the least efficient at low concentrations and had the lowest silica to alumina ratio, was most efficient at removing MTBE from water at concentrations above 100 mg/L. This difference in removal efficiency is believed to be attributed to the framework densities and the pore sizes of the zeolites. It is believed that zeolties with smaller pore sizes, i.e. larger framework densities, were better at removing MTBE at lower concentrations, and zeolites with larger pore sizes are more effective at higher concentrations [5].

Iron Catalyzed Oxidation Chemistry

In using traditional remediation technologies for the removal of MTBE from water, the contaminant is oftentimes transferred from the aqueous state to another phase. In contrast, Fenton's oxidation has been shown to mineralize MTBE as opposed to changing its phase. Oxidation using ferrous iron is an efficient method of removing organic compounds from water, but it requires the continuous addition of dissolved Fe^{2+}. However, there is an advantage in using solid, zero-valet iron, Fe^0 in lieu of ferrous iron because it can be attached to either stationary solids, such as filtration materials or it could be mobilized in soil grains in contaminated aquifers. In advanced oxidation, organic compounds are decomposed using hydroxyl radicals. These radicals have one unpaired electron, which makes them highly reactive, non-selective, and powerful in oxidation. In Fenton's oxidation process, hydroxyl radicals are produced from Fe^{2+} and hydrogen peroxide, H_2O_2. Bergendhal and Thies [6] found that Fenton's oxidation with Fe^0 removed over 99% of MTBE from water at pH 4.0 and 7.0 with a molar ratio of H_2O_2:MTBE of 220:1. The final acetone concentration produced by this process was reported as 400 µg/L, however, when a H_2O_2:MTBE molar ratio of 440:1 was used, the final acetone concentration was reported as 60 µg/L [6].

Synthesis Techniques

Basic zeolite synthesis is normally completed under hydrothermal conditions from solutions of sodium aluminate, sodium silicate, and sodium hydroxide for example. Such conditions are similar to those of the earth's crust, where natural zeolites were formed. The specific zeolite formed in a synthesis is dependent on the temperature, the pH, the amount of time allowed for the reaction, the reactants used, and the concentration in which the reactants are present. A typical range for incubation temperature is from 100°C to 200°C. In most syntheses, pH ranges from 10 to 14, and is often lowered during steps following synthesis. The most crucial factor in determining which zeolite will be produced is the template, which is usually an organic cation, around which the alumino-silicate lattice-structure is formed [7]. If a template is used during the synthesis, it must be removed by a calcination process. In this step, the zeolite is heated to a temperature, usually between 400°C and 600°C, at which the template decomposes and is released through the pores of the zeolite. For zeolites that are to be used as solid-state acids, the template must be replaced with hydrogen ions. For this application, the general post-synthesis treatment begins with the ion exchange of sodium with ammonium. Ammonia is then liberated by some type of heating, usually roasting, which leaves behind protons, giving the zeolite the needed acidic properties [7].

Ferrisilcate gels containing low molecular weight silica species can be used to synthesize the ferrisilicate molecular sieve analogues of the ZSM-5 zeolite. According to Szostak et al. [8], the three most crucial factors in the success of this synthesis are as follows: the prevention of iron hydroxide precipitation, the essentiality of the use of low molecular weight silica sources, and the suppression of the formation of iron complexes with organic amine crystal-directing agents. Since iron is capable of precipitating silica species through complex formation at pH

values between 3 and 4, the initial formation of the ferrisilicate complex must be completed at a low pH value to avoid the precipitation of iron hydroxide. Once the iron complexes are synthesized in this fashion, the formation of ferric hydroxide at elevated pH values is suppressed. The basic conditions needed for molecular sieve crystallization is achieved by adjusting the pH using the hydroxide ions found in sodium hydroxide. The ZSM-5 crystalline structure can be achieved with silica to iron ratios between 15 and 200, with the lower limit representing the amount of silica needed to react with all of the iron [8].

Another synthesis option that has been explored in recent years is that of ZSM-5 in fluoride media. In this type of synthesis, fluorides replace hydroxyl anions, which make it possible for synthesis to occur in neutral and slightly acidic media. The greatest advantage associated with using fluoride media as opposed to the conventional hydroxide ion solution is that the synthesis forms fewer metastable phases. This implies that any desired zeolite can be more easily prepared. Since this method forms larger crystals with few defects, the zeolites synthesized are ideal for studies of adsorption or diffusion [9]. Due to the neutral or slightly acidic nature of the medium used in this type of synthesis, elements that would otherwise be insoluble in alkaline media, such as Fe^{3+}, Ti^{4+}, and Co^{2+}, can be incorporated in the zeolite structure. Also, the ammonium form of ZSM-5 is formed directly by using NH_4F as the source of fluoride ions, as opposed to forming the Na-ZSM-5 intermediate, so that repeated ion exchange is not needed. The template can be simply burned off using calcination, and through this, the acidic zeolite form, H-ZSM-5 is created. Although the synthesis of zeolites using fluoride media has many advantages, which are stated previously, studies have shown that fluoride remains embedded in the zeolite structure after the calcination step, and due to fluorine's

high electronegativity, the electron densities around the neighboring silica are modified, which has the potential to cause modifications in the catalytic properties of the zeolite [9].

Seeding is another commonly used synthesis technique in the preparation of zeolites. Seeding is the process of adding crystals of the desired zeolite to synthesis batched in order to produce crystallization of specific zeolite phases. The method has also been known to increase the rate of crystallization during the synthesis. Research has shown that adding seeds also increases the birth rate of new zeolites and that both the crystallization rate and the birth rate increase with the amount of seeds added. Although these effects are advantageous for the synthesis of small zeolites, the average size of the zeolites produced decreases as the amount of seeds increases. With respect to seed size, smaller seeds have proven to be the most efficient in zeolite synthesis, as both the crystallization rate and the birth rate decrease as the seed size increases [10].

Exxon Process

The hydrocarbon conversion process is one in which zeolites have proven very useful. Exxon Research and Engineering Company obtained a recent patent for hydrocarbon conversion using a zeolite bound zeolite catalyst, as opposed to a zeoltie catalyst with an amorphous binder. This allows the zeolites to convert hydrocarbons at a higher rate of adsorption. Exxon uses a three step process to prepare these catalysts, specifically the MFI zeolite. First, a solution which contains tetrapropyl ammonium hydroxide (TPAOH) or bromide (TPABr), alkali metal oxide, an oxide of aluminum, an oxide of silicon, and water is prepared and heated to a temperature within the range of 80° C to 200° C for a period of about four hours to eight days. Solid crystal particles are formed from the resulting gel, which are separated from the reaction media, washed and dried. The calcination step for this synthesis is optional, but is performed in air at

temperatures of approximately 400° C to 550° C for a period of approximately 10 to 40 hours to remove the TPA ions. Next, a silica-bound zeolite is prepared by creating a mixture comprised of the zeolite crystals, a silica gel or sol, water, and optionally and extrusion aid to produce a homogeneous extrudable paste. Silica sol containing less than 1000 ppm of alumina is the preferred silica binder. An amount of silica corresponding to a zeolite content of preferably 55 to 85% by weight is used, with the balance being predominately silica. The paste is then extruded and cut into extrudates that are 2mm in diameter. These are dried at temperatures of 100° C to 150° C for a period of approximately 4-12 hours. The dried extrudates are then calcined at temperatures of about 400° C to 550° C for 1-10 hours to destroy the extrusion aid. The final step in the catalyst synthesis process is to convert the silica in the silica-bound zeolite to a second zeolite. The resulting catalyst should contain preferably less than 3% of a non-zeolitic binder based on the weight of both zeolites. The silica-bound aggregate is aged in a solution with a molar OH^-:SiO_2 ratio within the range of 0.07 to 0.15 at elevated temperatures in the range of approximately 145° C to 155° C for approximately 70 to 80 hours. After aging, the zeolite is removed from the solution and washed, dried, and calcined. A solution of NaOH (aq) and TPABr is mixed, and the silica-bound extrudate is added. The composition is then heated to approximately 150° C and maintained at this temperature for 70 to 80 hours. The resulting product is then washed, dried, and calcined at a temperature in the range of 450° C to 550° C to remove TPA ions. The zeolite may then be ion exchanged based on application [11].

Prior MQP Results

Spence Konde also used aged solutions in his synthesis of zeolites. Unlike many syntheses, Konde utilized silica beads, as opposed to silica gel. To prevent cracking, the beads were cured by being placed in a small beaker, which was in turn placed in a larger beaker that contained water. The large beaker was sealed with Parafilm and allowed to sit for 2 weeks. First, he mixed a solution of TPABr and NaOH with a ratio of 7:1 and added DI water. The solution was then divided into eight samples. To four of the samples, silica beads were added, and all of them were set aside for 24 hours. After aging, silica beads were added to the other four samples. The samples were heated to 130° C, and were removed at 7, 10, 14, and 18 days. The samples were quenched in a cold water bath and dried using a Buchner funnel. No calcination was performed in any of Konde's syntheses [12].

The 7 and 10 day samples of Konde's synthesis were all reported to have a thin crystalline coating, with the beads having strengths consistent with those of unconverted silica beads. There was no powder present in the samples, and the beads were only slightly stuck together. The 14 day samples had crystalline coatings similar to those in the 7 and 10 day samples, however, in contrast, the underlying unconverted portion of the samples only constituted 40-75% of the bead by volume with powder found in the samples. Higher conversions were observed in the pre-aged samples. The 18 day samples showed a much higher conversion than the earlier samples. Both the pre-aged and the non-pre-aged samples showed nearly complete conversion. In the pre-aged sample, most of the completely converted beads were hollow [12].

It was concluded that the best method of conversion of silica beads to zeolites was via the hydrothermal treatment at 130° C for 18 days. For maximum conversion, samples must be pre-

aged in the synthesis mixture at room temperature before beginning the hydrothermal treatment. Although no agitation was preformed during the synthesis, it is believed that mild agitation would produce better results [12].

This study will serve as a continuation of Konde's work. Insight from Konde's experiments will be used to develop a viable hydrothermal synthesis procedure to incorporate iron into ZSM-5.

Methodology

Synthesis Run 1 (Oven with Rotisserie)

A solution of approximately 7.67 g of Fe_2O_3, 21.19 mL of HNO_3 (aq) (EM Science 70%), and 2.0 g of TPABr (Fluke 98+ %) was prepared in 100 mL of DI water. Into each of two Teflon-lined steel autoclaves, 5 mL of the previously mentioned solution along with 5.7 g of cured silica beads (t.h.e. desiccant, EM Science) were added. The mole oxide formula was 1.0 SiO_2 0.03 Fe_2O_3 0.23 HNO_3 0.0068 TPABr 3.89 H_2O. The autoclaves were sealed and set aside for 24 hours. After the pre-aging, the autoclaves were placed in an oven with a rotisserie to facilitate agitation at 150° C. The autoclaves were removed at 5 days and 10 days. The samples were quenched by placing the autoclaves in a cold water bath, and the contents filtered using a Büchner funnel. The liquid was discarded, and the samples were washed twice with DI water.

Synthesis Run 2 (Conventional Oven)

A solution of 0.2 g Fe_2O_3, 1 mL of HNO_3 (aq), and 0.75 g TPABr was prepared in 15 mL of DI water. To a Teflon-lined steel autoclave, 0.51 g of silica gel beads were added, followed by 1 mL of solution. A solution of 40.0 g NaOH (Aldrich, ACS 97+ %) was prepared in 1 L of DI water, and 0.5 mL was added to the autoclave. The mole oxide formula was 1.0 SiO_2 0.0084 Fe_2O_3 0.11 NaOH 0.12 HNO_3 0.034 TPABr 6.88 H_2O. An additional 2 drops of DI water was added to the solution in the autoclave to preserve the composition of the solution as water evaporated during the synthesis. The autoclave was sealed and set aside for 24 hours. After the pre-aging the autoclave was placed in a conventional oven at a temperature of 170° C for 5 days. The sample was quenched in a cold water bath, and the liquid was discarded. The contents were washed and filtered with DI water and a Büchner Funnel 5 times and were dried at 100° C for 8 hours.

Synthesis Run 3

A solution of 0.2 g Fe_2O_3, 1 mL of HNO_3 (aq), and 0.75 g TPABr was prepared in 15 mL of DI water. Approximately 0.50 g of silica gel beads were added to each of three Teflon-lined steel autoclaves, followed by 1 mL of solution. The NaOH solution from synthesis run 2 was used again for this run, and 0.5 mL was added to each autoclave. 1.0 SiO_2 0.0084 Fe_2O_3 0.11 NaOH 0.12 HNO_3 0.034 TPABr 6.88 H_2O. An additional 2 drops of DI water were added to the solution in each autoclave to preserve the composition of the solution as water evaporated during the synthesis. The autoclaves were sealed and set aside for 48 hours. After the pre-aging the autoclave was placed in a conventional oven at a temperature of 170° C. The autoclaves were removed at 5, 10, and 15 days. The samples were quenched in a cold water bath, and the liquid was discarded. The contents were washed and filtered with DI water and a Büchner Funnel 5 times and were dried at 100° C for 24 hours.

Synthesis Run 4

A solution of 0.4 g Fe_2O_3, 1 mL of HNO_3 (aq), and 0.75 g TPABr was prepared in 15 mL of DI water. Approximately 0.50 g of silica gel beads were added to each of three Teflon-lined steel autoclaves, followed by 1 mL of solution. The NaOH solution from synthesis run 2 was used again for this run, and 0.5 mL was added to each autoclave. 1.0 SiO_2 0.016 Fe_2O_3 0.11 NaOH 0.12 HNO_3 0.034 TPABr 6.88 H_2O. An additional 2 drops of DI water was added to the solution in each autoclave to preserve the composition of the solution as water evaporated during the synthesis. The autoclave was sealed and set aside for 48 hours. After the pre-aging the autoclaves were placed in a conventional oven at a temperature of 170° C. The autoclaves were removed at 5, 10, and 15 days. The samples were washed and filtered with DI water and a Büchner Funnel 5 times and were dried at 100° C for 24 hours.

Results and Discussion

Synthesis Run 1

After inspection under an optical microscope, it was determined that the samples from this synthesis were completely unconverted. The iron was observed to have dried on the outside of the beads. It was suspected that the acidic conditions of the solution prohibited the nucleation step of the conversion. The temperature of the oven used was difficult to stabilize; therefore a test run was completed to determine whether an oven without a rotisserie would produce viable results.

Synthesis Run 2

Upon visual inspection, it was observed that all of the beads remained intact during the synthesis. All beads were white and opaque, and some beads had a red residue on the outside.

Through examination under an optical microscope, it was determined that a limited number of crystals were present in the sample. Since crystals were present, the sample was analyzed in a scanning electron microscope. It was believed that an increase in both pre-aging and synthesis time would increase the number of crystals present in the sample. It was determined through SEM analysis that zeolite crystals only grew on part of the beads, and those surfaces that contained crystals, the crystalline material seemed scattered with many gaps and inconsistencies as shown in figures 1-6. This is suspected to be due to the fact that the entire surface of each bead may not have been completely covered in solution. During the pre-aging process, the iron added to the solution settled at the bottom of the autoclave. Although the solution was stirred after the pre-aging process and before the autoclave was placed in the oven, it is suspected that it settled during the synthesis as well and hindered the synthesis process on the bottom of the bead. EDX elemental analysis showed that Fe species were present in the

zeolite samples with a weight percent of 31.00 on the surface, while the silica species had a weight percent of 24.32. Although there was a large concentration of iron on the surfaces of the beads, there was a clear lack of crystals. From this, it was determined that the iron compounds were fused into the amorphous coating of the beads, rather than incorporated into the crystals themselves. With the results of this test run, it was determined that a conventional oven would suffice for all future runs, but more pre-aging time was needed to produce more crystals. All other runs were pre-aged for 48 hours.

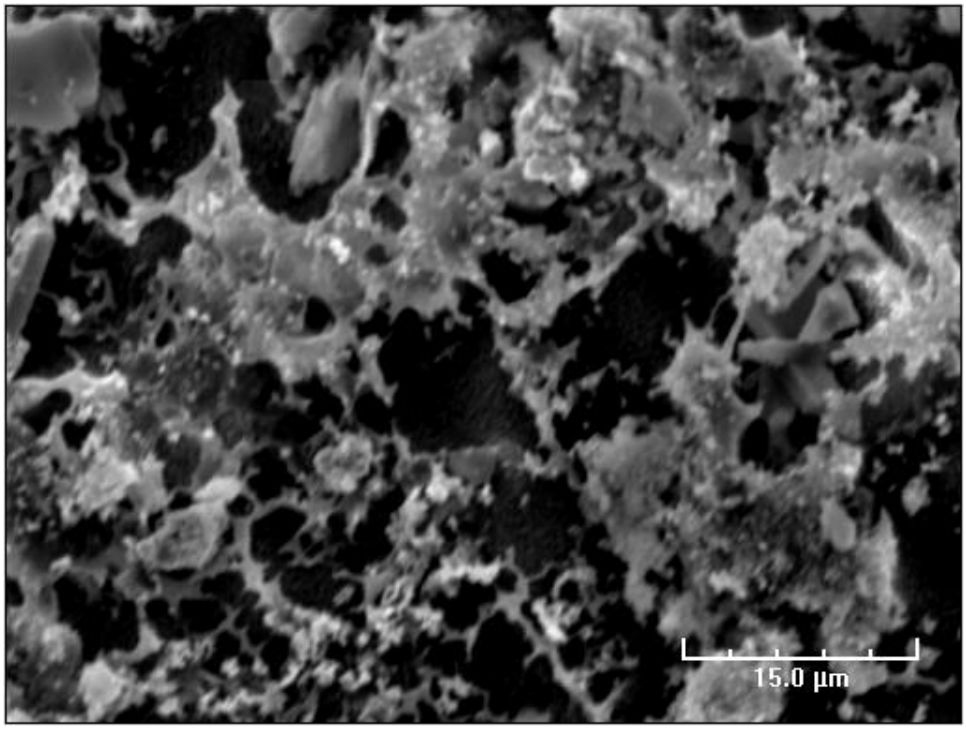

Figure 1: Synthesis Run 2, 2 kX (Scarce Number of Crystals)

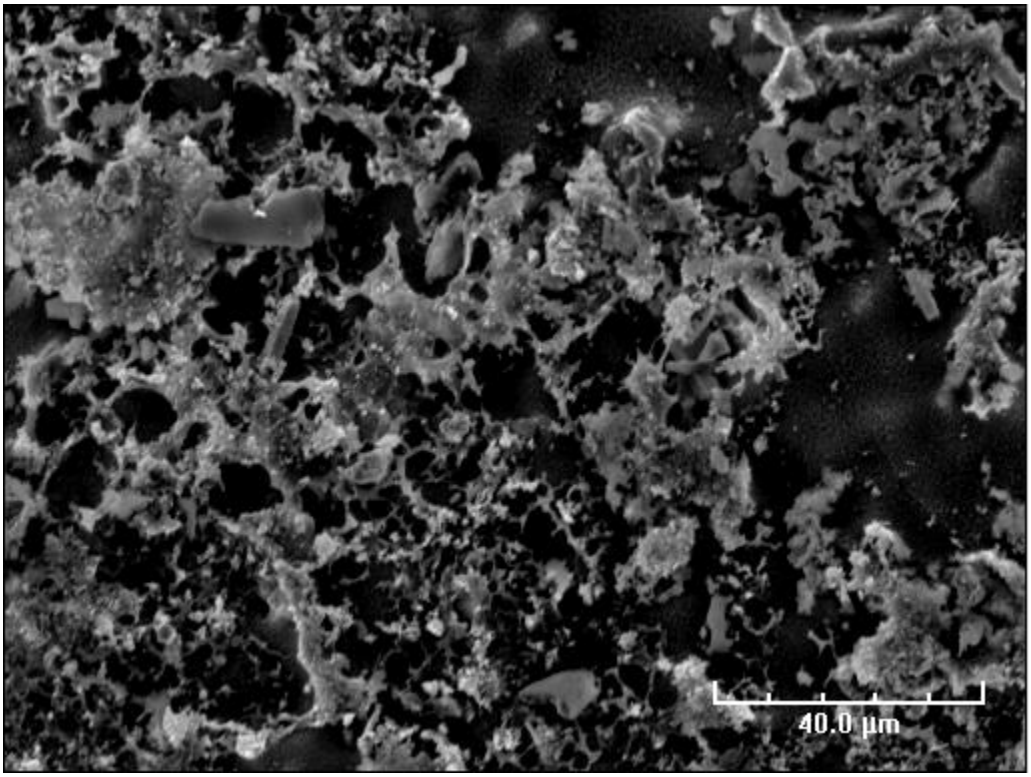

Figure 2: Synthesis Run 2, 1 kX (Scattered Crystalline Material)

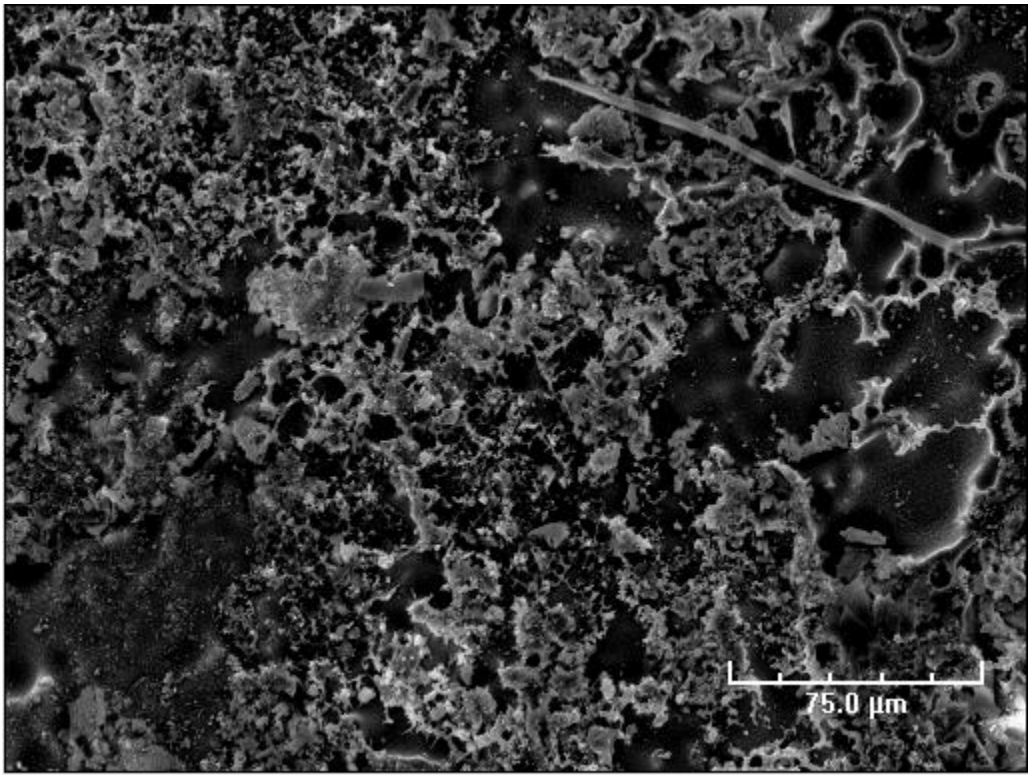

Figure 3: Synthesis Run 2, 0.5 kX

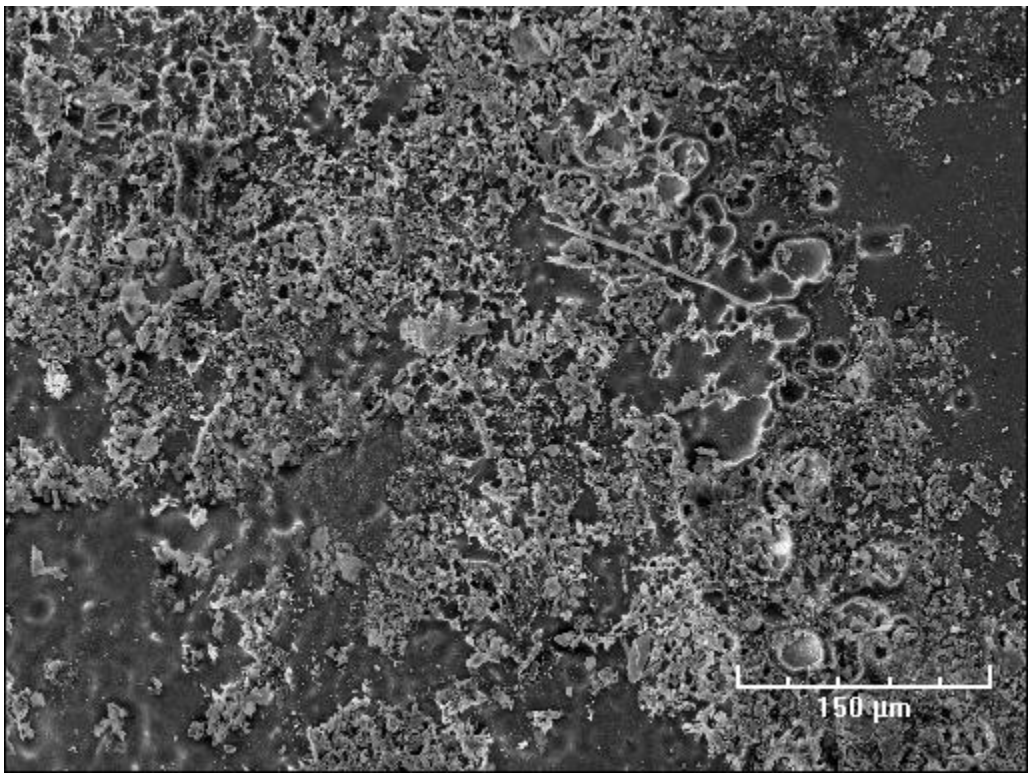

Figure 4: Synthesis Run 2, 0.25 kX

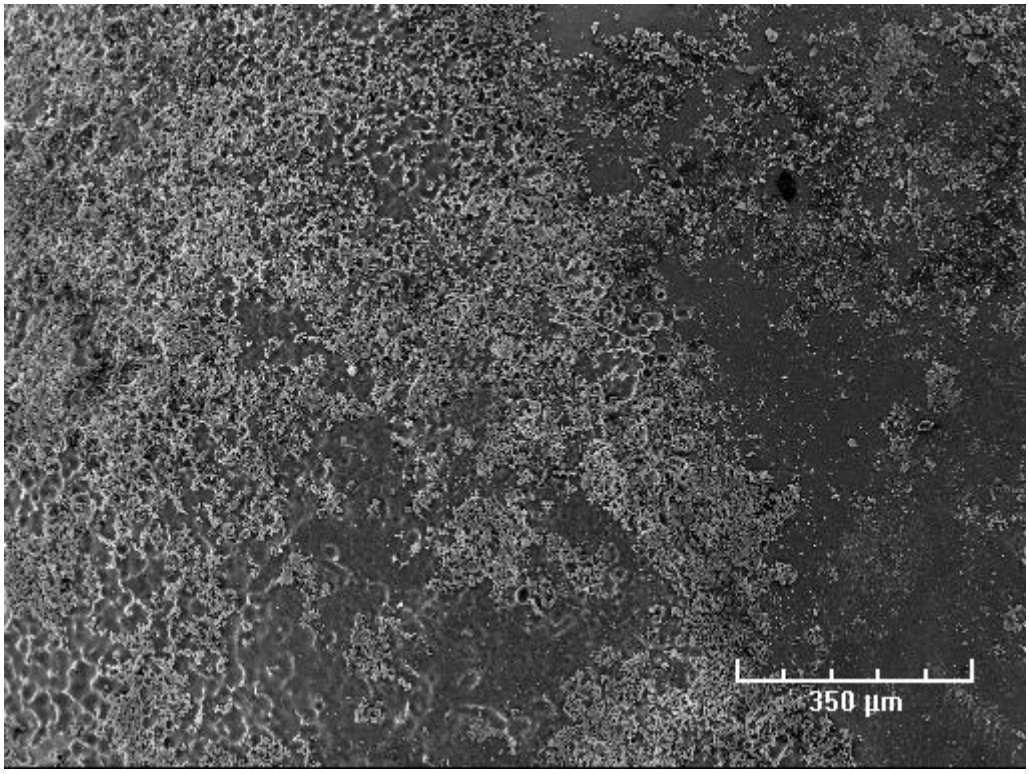

Figure 5: Synthesis Run 2, 0.1 kX

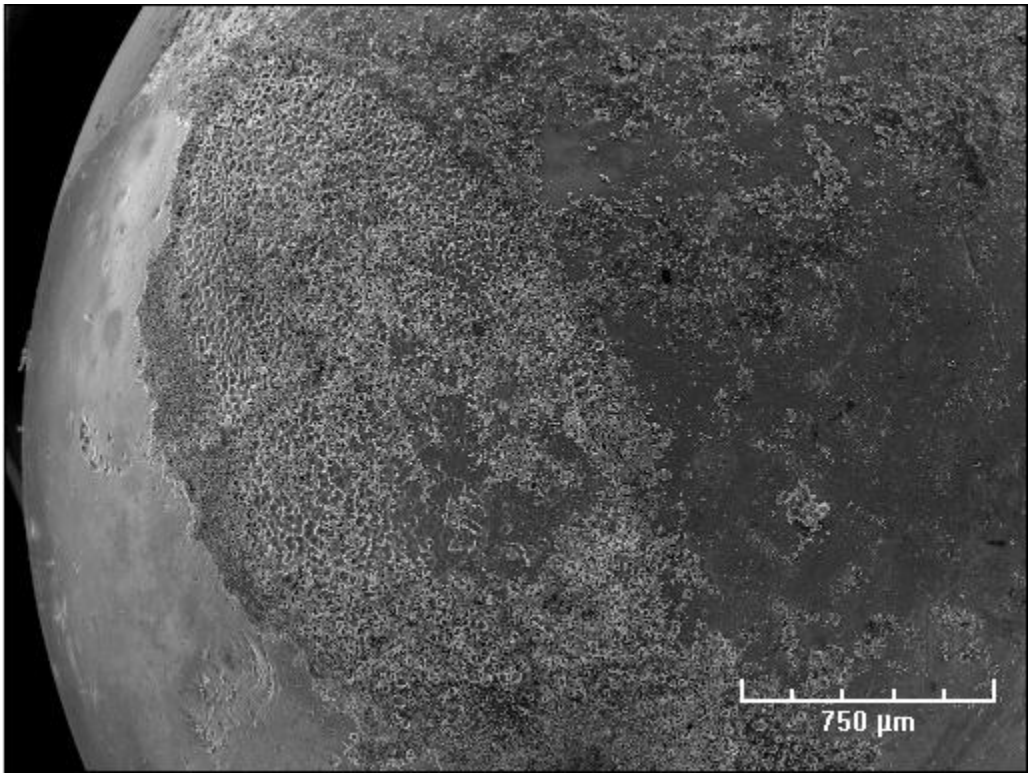

Figure 6: Synthesis Run 2, 0.05 kX (Crystalline Material Restricted from Bottom of Bead)

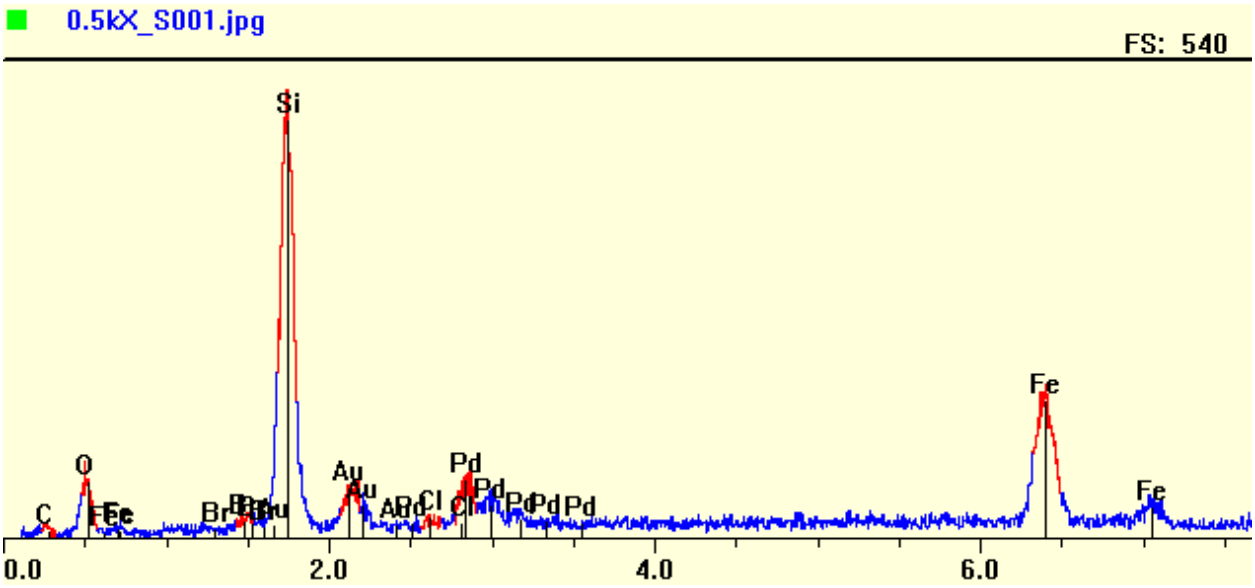

Figure 7: Synthesis Run 2, 0.05 kX (EDX)

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
Si	KA1	1.740	0.1943	24.32	27.30	1.70
O	KA1	0.523	0.1087	25.28	49.83	3.25
C	KA1	0.277	0.0000	0.00	0.00	0.00
Fe	KA1	6.403	0.2836	31.00	17.51	0.94
Br	LA1	1.480	0.0113	1.76	0.70	1.70
Cl	KA1	2.622	0.0000	0.00	0.00	0.00
Pd	LA1	2.838	0.1020	13.47	3.99	1.70
Au	MA1	2.123	0.0251	4.16	0.67	1.70
Total				**100.00**	**100.00**	**1.38**

Figure 8: Synthesis Run, 2, 0.05 kX (EDX elemental analysis)

Synthesis Run 3

Upon visual inspection, it was observed that all beads remained intact throughout the synthesis. The beads from the 5 day sample were observed to be white and opaque, while a visible trace of red residue was present on the outside of the beads from the 10 day sample. Beads from the 15 day sample seemed to be white on the outside with red specks on some beads.

Through examination under an optical microscope, it was determined that a limited number of crystals were present in the 5 day sample. A large number of red particles seemed to be present in the 10 day sample. The 15 day sample seemed to have produced an adequate number of red particles as well, however not as many as yielded by the 10 day sample. It was determined through SEM analysis that the largest crystals were in the 5 day sample, and opposed to existing crystals growing in size with incubation time; there was evidence that more nucleation took place. Although the 5 day sample had large crystals, the number of crystals appeared to be fewer than those of the 10 and 15 day samples. As shown in Figure 11, it appears as if during the incubation time of the 10 day sample that the beads became stuck together, which resulted in the damaging of the coating in removal and handling and possible the inhibition of crystals to grow larger. The 15 day sample also showed signs of damaged coating, but the coating that remained intact appeared to be comprised of mostly very small crystals. Although in the 15 day sample there were some crystals comparable in size to those in the 5 day sample, the number of large crystals was greatly reduced.

EDX elemental analysis showed that iron species were indeed present in all of the samples at low concentrations. In the 5 day sample iron was 1.02 wt. % of the sample, compared to silica species at 40.45 wt. %. The analysis of the 10 day sample showed an iron composition of 3.30 wt. % and a silica composition of 39.82 wt. %. Iron made up 0.68% of the 15 day

sample by weight, as opposed to silica species 35.80 at 35.80%. It was also notice that as the iron percentage decreased the percentage of oxygen present in the samples consistently increased. Although XRD analyses were preformed for the samples in this run, peaks were difficult to place in the analyses of the scans for this run. XRD analysis suggested that various ferrous silicate oxides were present in all samples from run 3, though results were not definite.

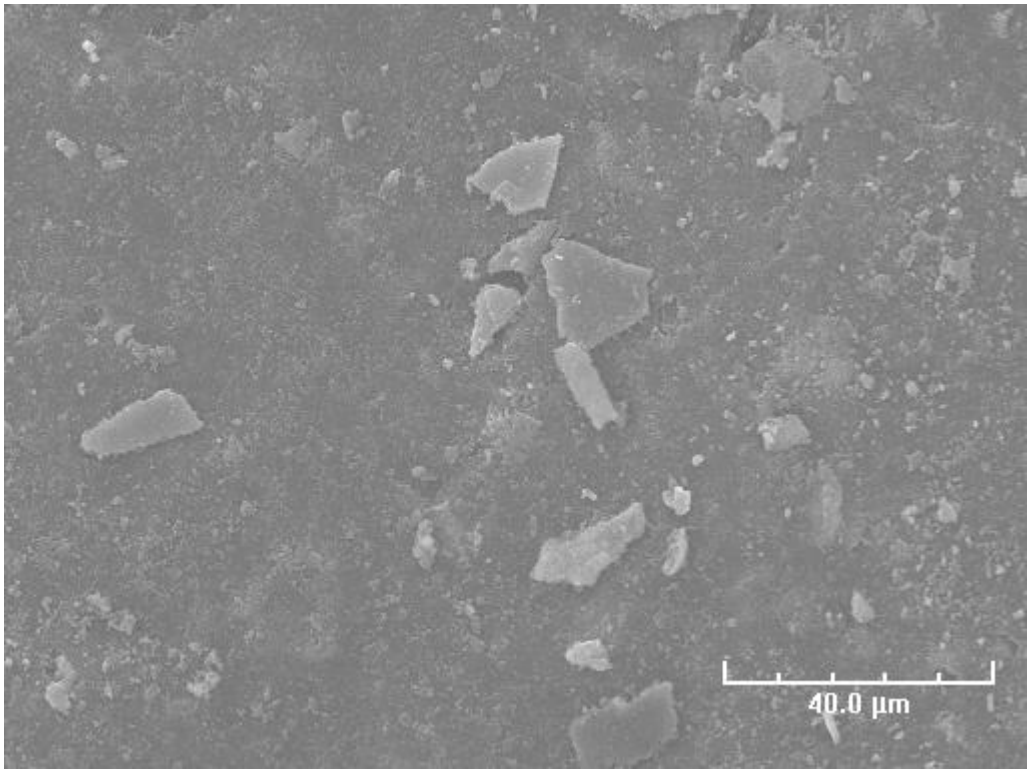

Figure 9: Synthesis Run 3, Day 5, 1 kX (Large Crystals)

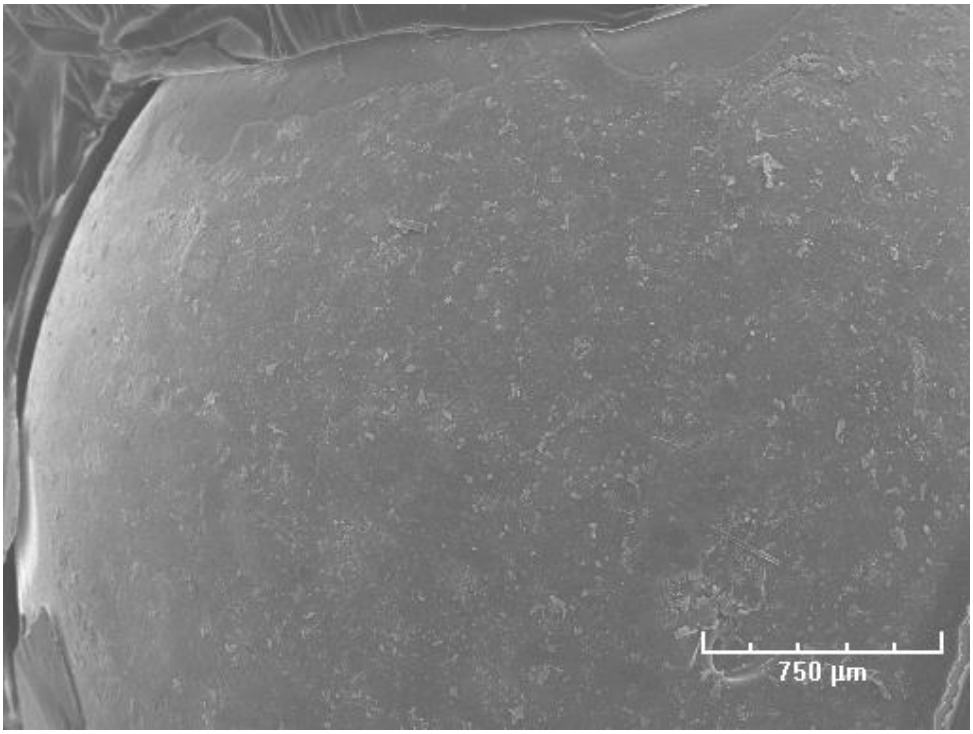

Figure 10: Synthesis Run 3, Day 5, 0.05 kX (Thin crystalline layer)

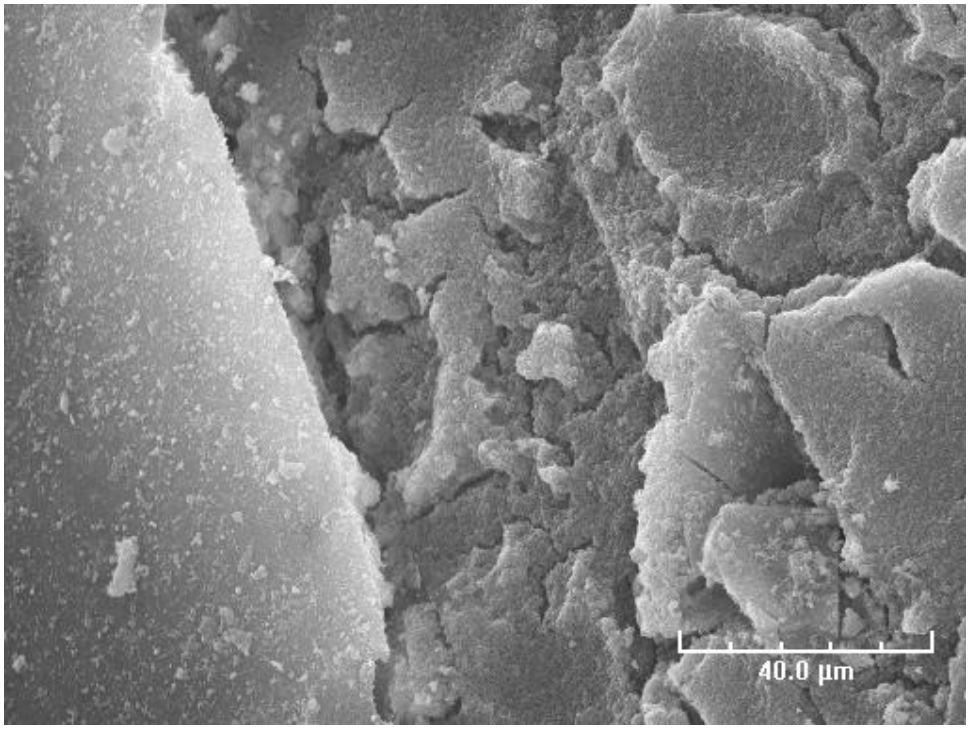

Figure 11: Synthesis Run 3, Day 10, 1 kX (Area shown where bead was stuck to another bead)

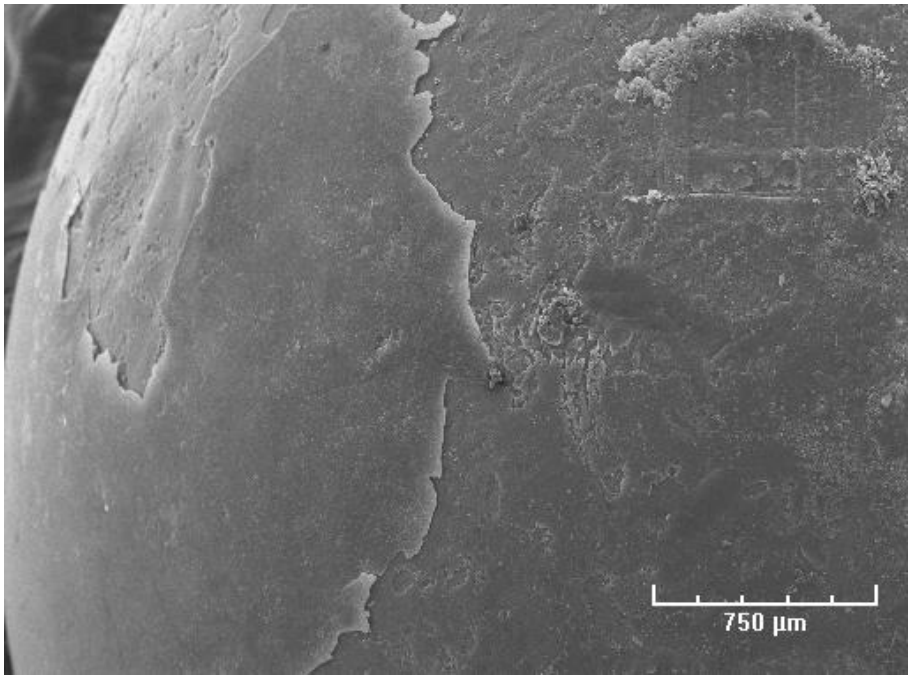

Figure 12: Synthesis Run 3, Day 10, 0.05 kX (Damaged Coating)

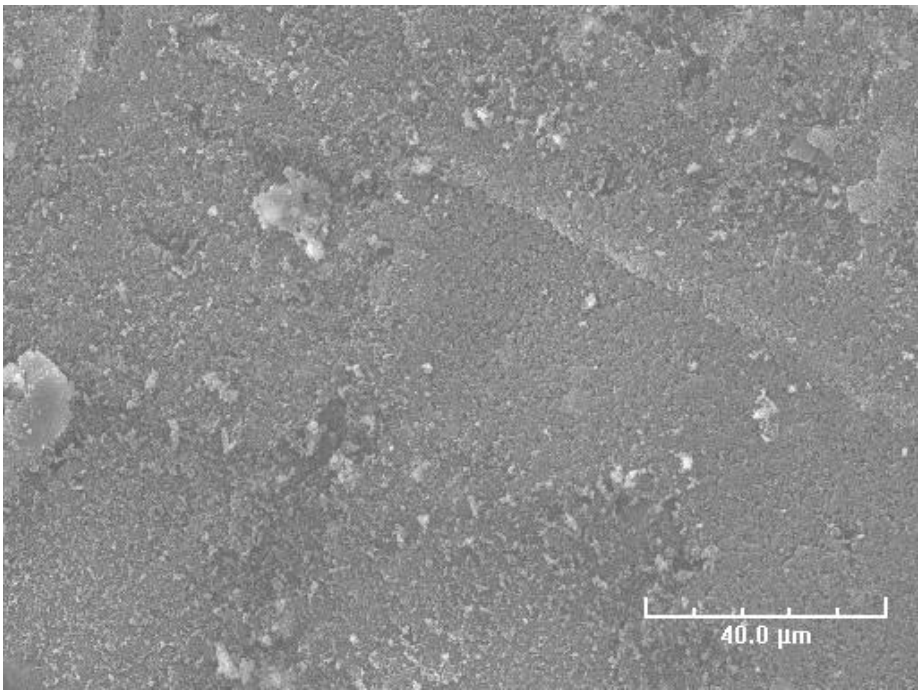

Figure 13: Synthesis Run 3, Day 15, 1 kX (Large crystals surrounded by small ones)

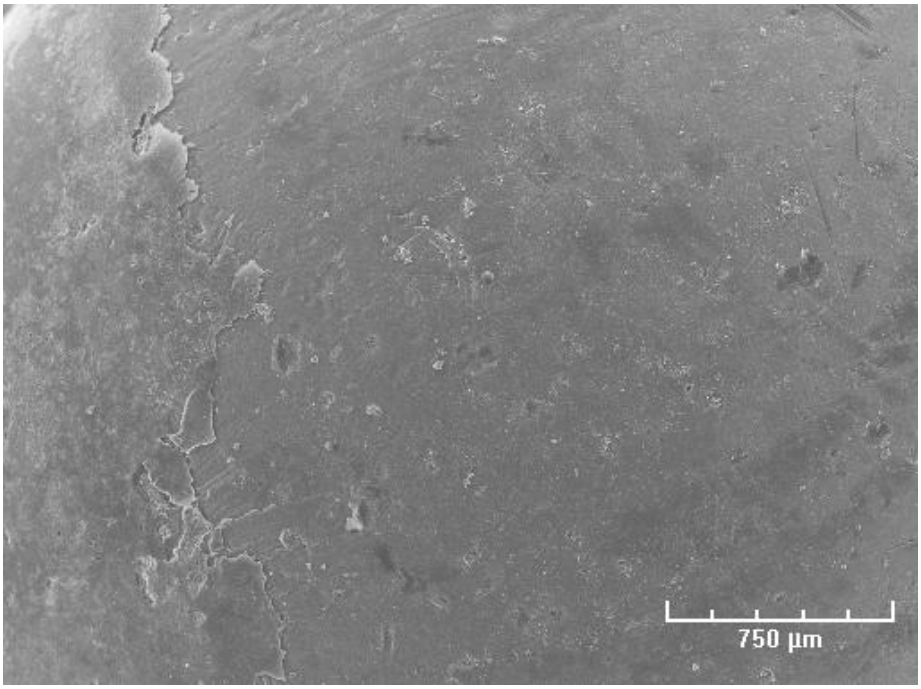

Figure 14: Synthesis Run 3, Day 15, 0.05 kX (Damaged Coating)

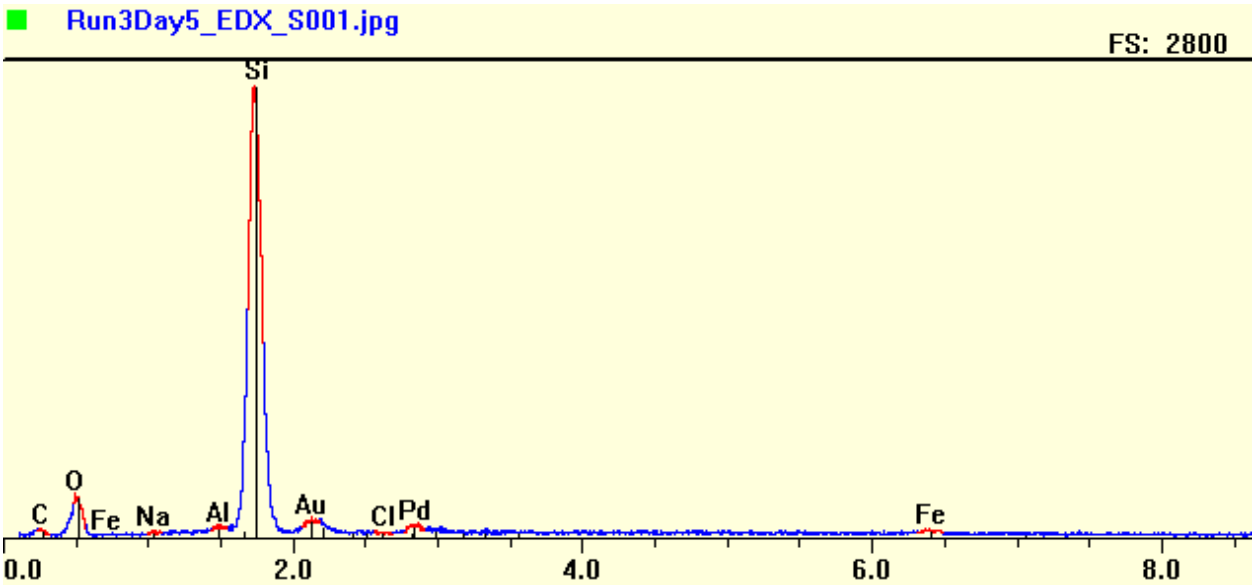

Figure 15: Synthesis Run 3, Day 5 (Global EDX)

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
C	KA1	0.277	0.0000	0.00	0.00	0.00
O	KA1	0.523	0.1365	50.81	67.51	11.03
Si	KA1	1.740	0.3441	40.45	30.62	1.58
Fe	KA1	6.403	0.0085	1.02	0.39	1.08
Pd	LA1	2.838	0.0240	3.82	0.76	1.58
Al	KA1	1.487	0.0035	0.44	0.35	1.58
Au	MA1	2.123	0.0159	3.46	0.37	1.58
Cl	KA1	2.622	0.0000	0.00	0.00	0.00
Na	KA1	1.041	0.0000	0.00	0.00	0.00
Total				**100.00**	**100.00**	**1.84**

Figure 16: Synthesis Run 3, Day 5 (EDX Elemental Analysis)

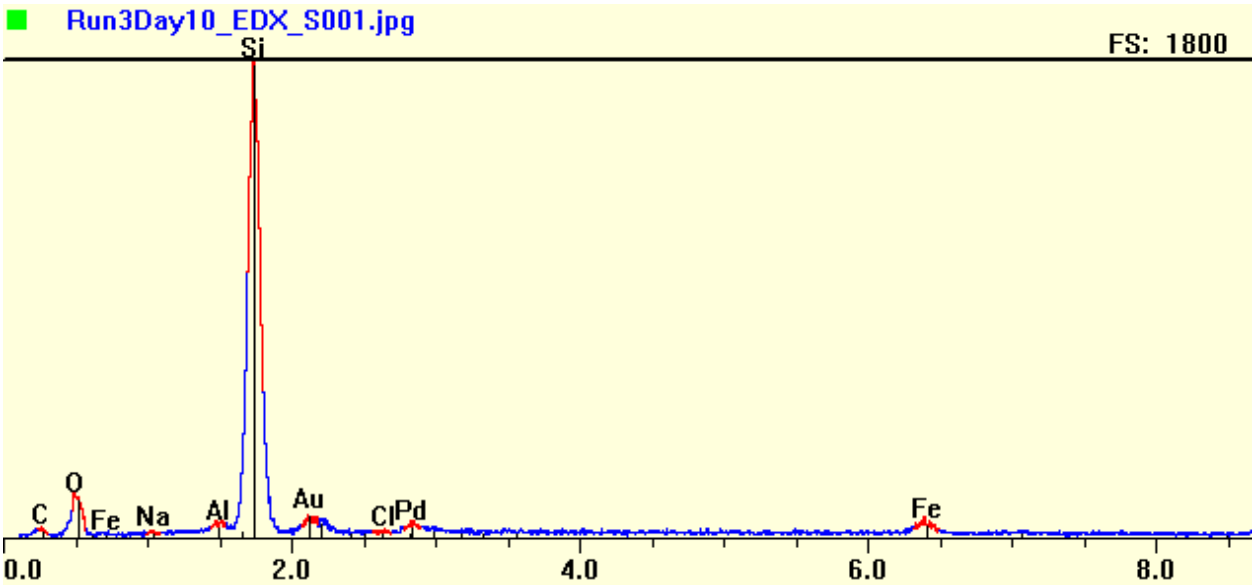

Figure 17: Synthesis Run 3, Day 10 (Global EDX)

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
C	KA1	0.277	0.0000	0.00	0.00	0.00
O	KA1	0.523	0.1331	48.54	66.03	6.84
Si	KA1	1.740	0.3296	39.82	30.86	1.30
Fe	KA1	6.403	0.0276	3.30	1.28	0.96
Pd	LA1	2.838	0.0274	4.30	0.88	1.30
Al	KA1	1.487	0.0054	0.72	0.58	1.30
Au	MA1	2.123	0.0156	3.33	0.37	1.30
Cl	KA1	2.622	0.0000	0.00	0.00	0.00
Na	KA1	1.041	0.0000	0.00	0.00	0.00
Total				**100.00**	**100.00**	**1.46**

Figure 18: Synthesis Run 3, Day 10 (EDX Elemental Analysis)

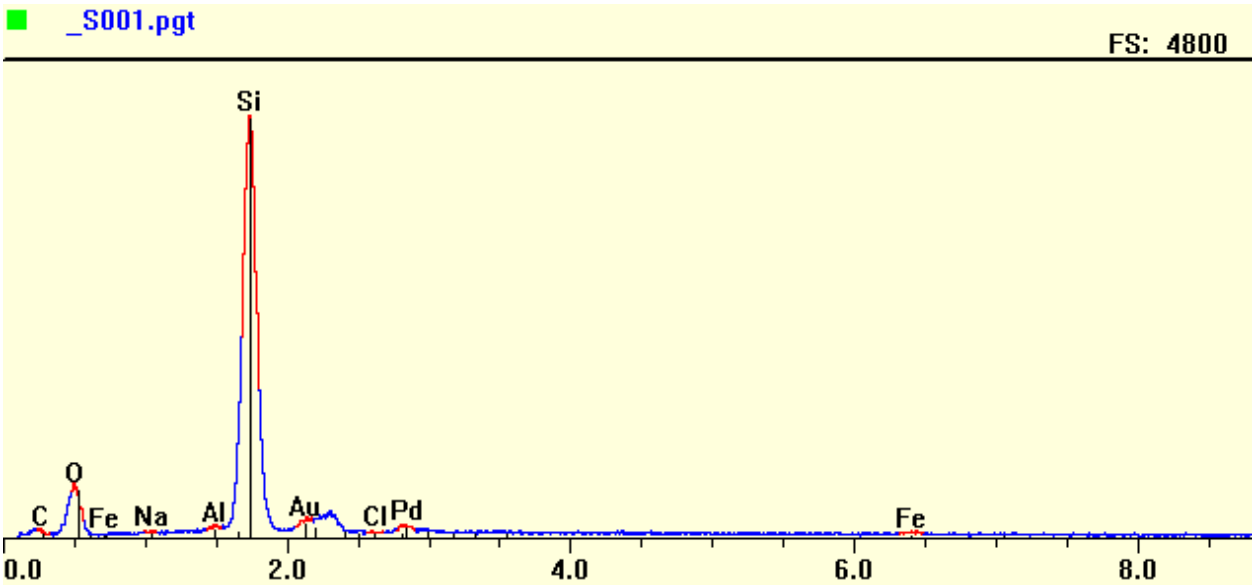

Figure 19: Synthesis Run 3, Day 15 (Global EDX)

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
Na	KA1	1.041	0.0000	0.00	0.00	15.10
C	KA1	0.277	0.0000	0.00	0.00	11.84
O	KA1	0.523	0.1617	56.63	72.45	46.17
Cl	KA1	2.622	0.0000	0.00	0.00	11.84
Si	KA1	1.740	0.2984	35.80	26.09	17.86
Al	KA1	1.487	0.0025	0.33	0.25	17.86
Fe	KA1	6.403	0.0056	0.68	0.25	0.99
Pd	LA1	2.838	0.0201	3.17	0.61	17.86
Au	MA1	2.123	0.0160	3.38	0.35	17.86
Total				**100.00**	**100.00**	**14.63**

Figure 20: Synthesis Run 3, Day 15 (EDX Elemental Analysis)

Synthesis Run 4

Upon visual inspection, it was observed that all beads remained intact during the synthesis. White and opaque beads were observed in the 5 day sample, while beads from the 10 day sample contained nearly and entirely red surface. The beads from the 15 day sample were white on the outside with what seemed to be an underlying red layer in some beads and a red spot on the outside of others.

Through examination under an optical microscope, it was determined that a limited number of red particles were present in the 5 day sample. The 10 and 15 day samples seemed highly concentrated with red particles, with the 10 day having the largest of the three samples. The particles were confirmed to be crystals using SEM analysis. Using SEM analysis, it was determined that the 5 day sample contained very few crystals, and parts of the coating may have been damaged during the removal of the beads, as the surface looked highly inconsistent. The 10 day sample contained very many fairly large crystals, and though this sample had fewer inconsistencies than the 5 day sample, there were still some inconsistencies in texture on the surface of the bead, which is again believed to be due to damage during its removal and handling. The 15 day sample had crystals which were much smaller than those in the 10 day sample, but there were, by far, more crystals on the surface of the bead. Like the 5 and 10 day samples, there appeared to be a portion of the crystalline coating of the bead that was damaged or removed as it was handled. The portion of the surface which remained intact seemed to have a consistent concentration of crystals which were close in size.

EDX elemental analysis showed that iron was again present in low concentrations in all of the samples. Iron made up 2.61% of the 5 day sample by weight, with silica species occupying 41.68%. The 10 day sample, like that of run 3, contained the most iron, which in this

case was 7.19 wt. % with a silica percentage of 34.42. Also consistent with its respective sample from run 3, the 15 day sample contained the least weight percentage of iron, which was 1.21, with 37.13 wt. % of the surface consisting of silica species. The percentages of iron in the samples from this run were consistent with the fact that twice as much iron was used in samples from run 4 as those in run 3. As in run 3, various ferrous silicate oxides were present in all samples according to XRD analysis, but no definite results were obtained using this method of analysis.

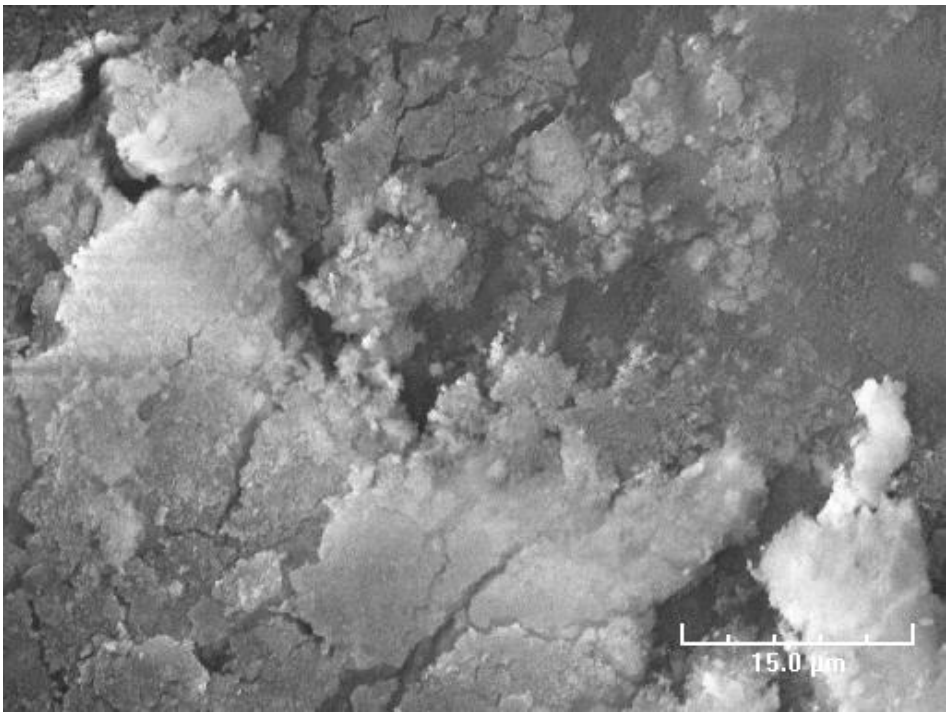

Figure 21: Synthesis Run 4, Day 5, 2 kX (Inconsistent Surface)

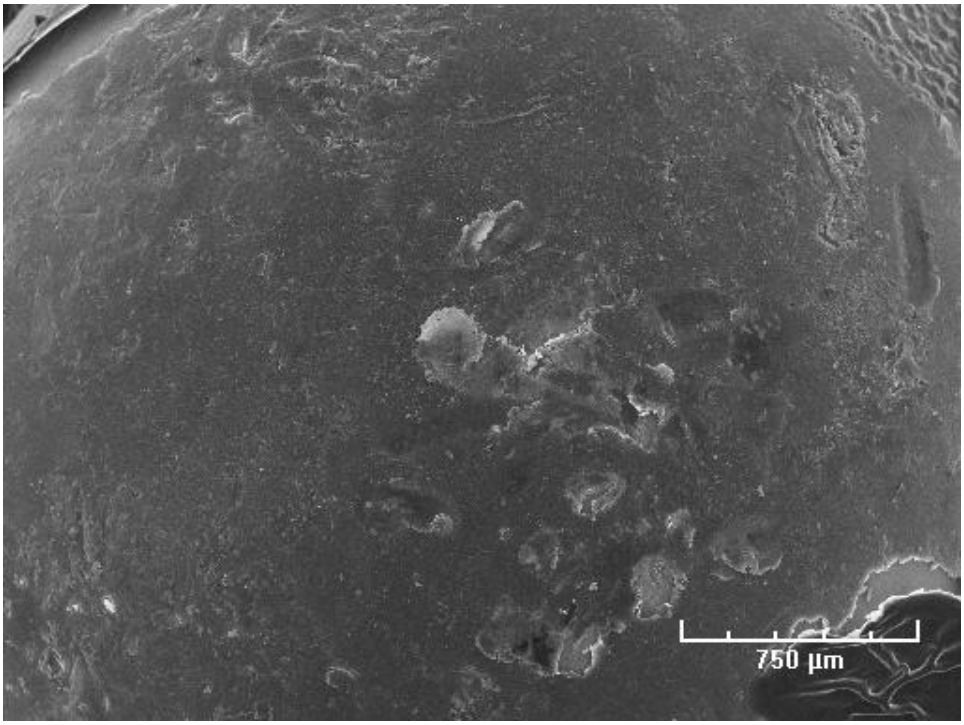

Figure 22: Synthesis Run 4, Day 5, 0.05 kX (Damaged Coating)

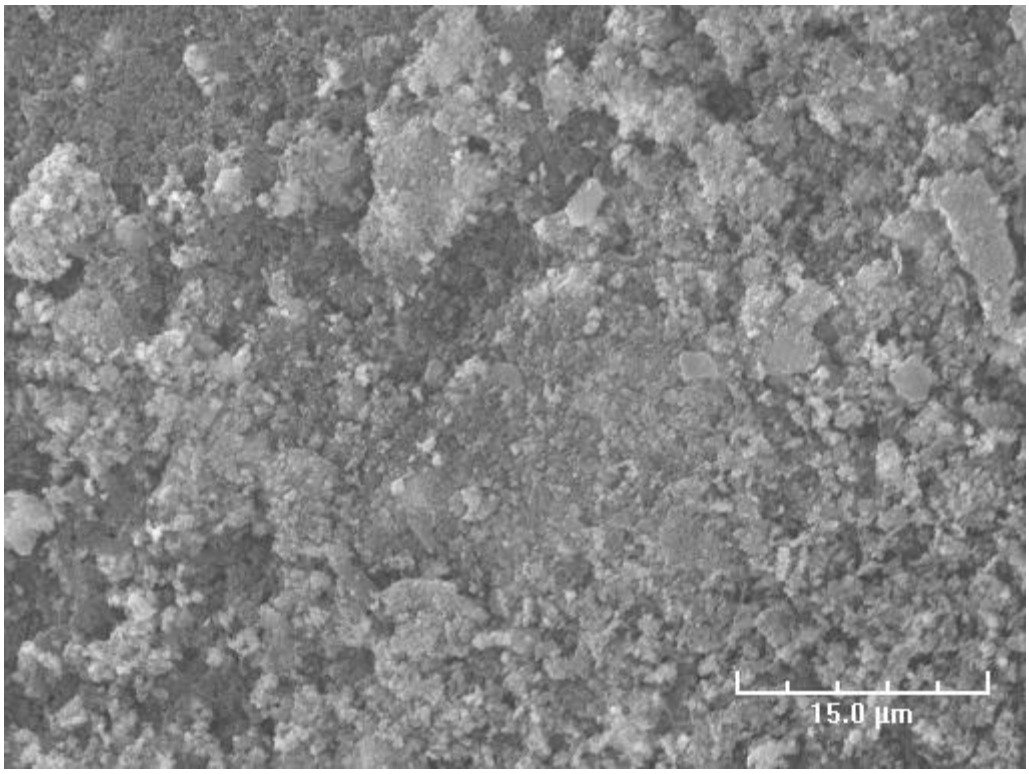

Figure 23: Synthesis Run 4, Day 10, 2 kX (Larger more concentrated crystals)

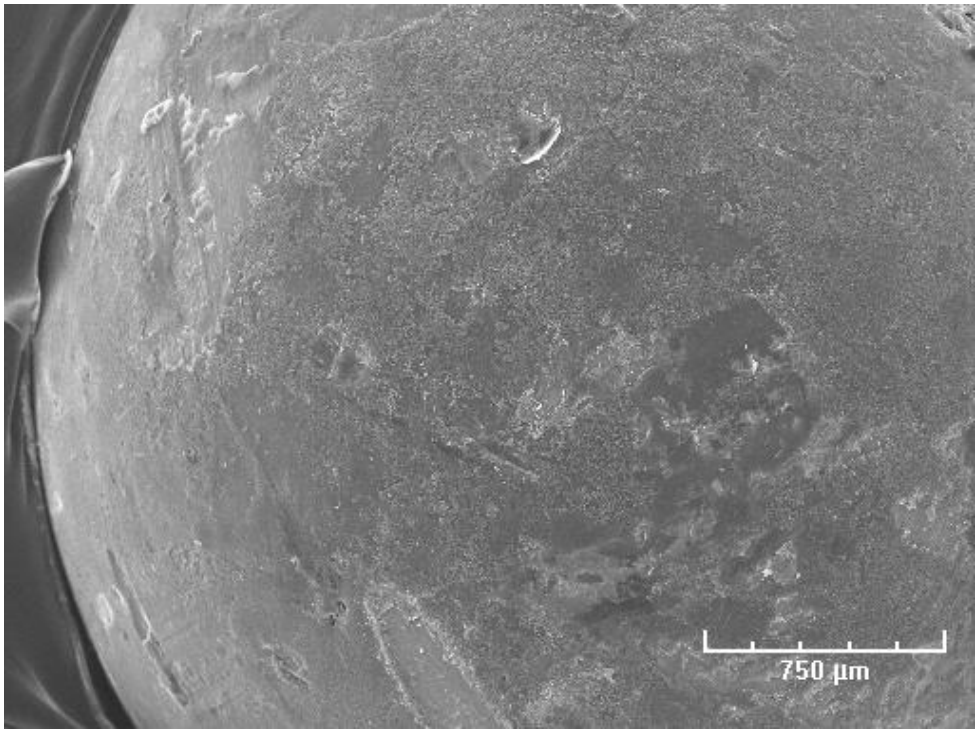

Figure 24: Synthesis Run 4, Day 10, 0.05 kX (Damaged Coating)

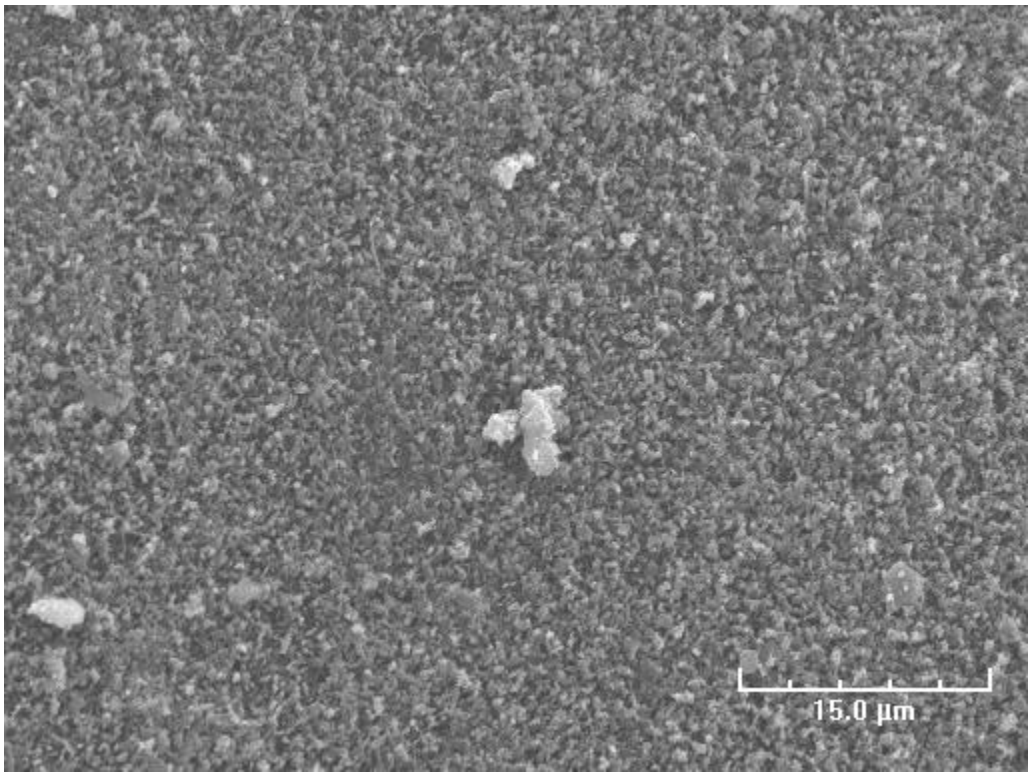

Figure 25: Synthesis Run 4, Day 15, 2 kX (Smaller more concentrated crystals)

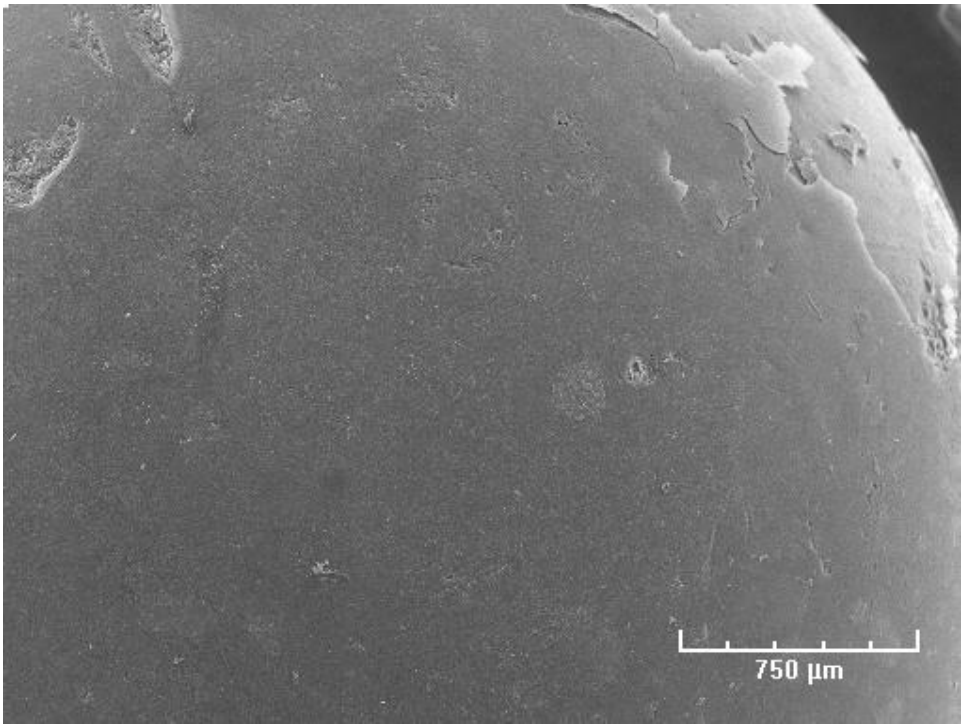

Figure 26: Synthesis Run 4, Day 15, 0.05 kX (Damaged Coating)

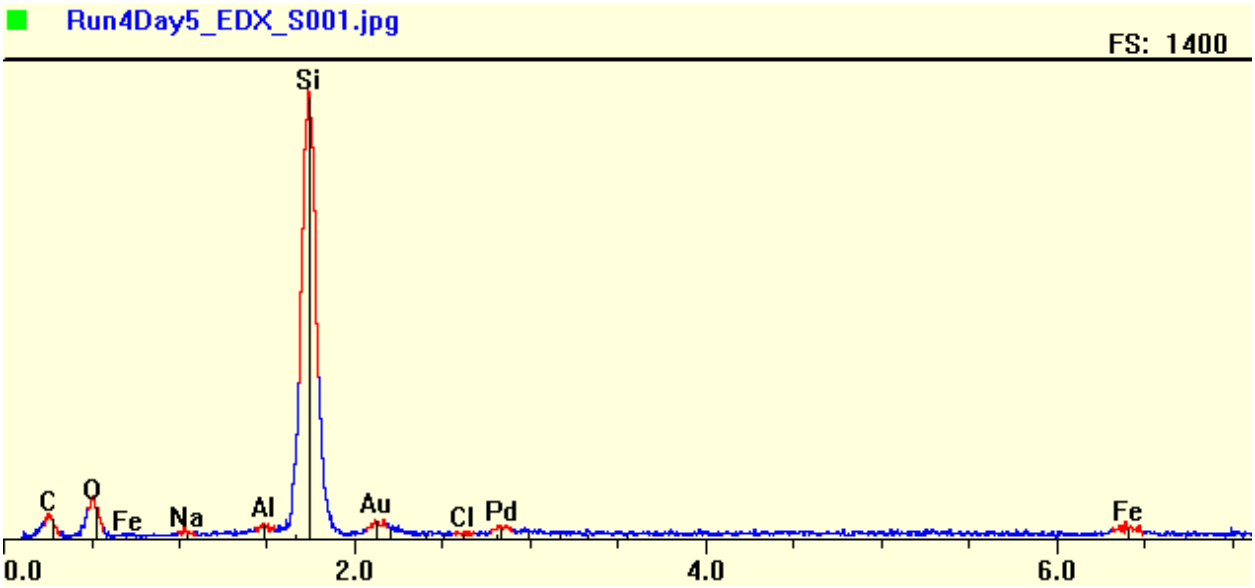

Figure 27: Synthesis Run 4, Day 5 (Global EDX)

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
C	KA1	0.277	0.0000	0.00	0.00	1.45
O	KA1	0.523	0.1320	48.29	65.17	4.94
Si	KA1	1.740	0.3499	41.68	32.05	1.68
Fe	KA1	6.403	0.0219	2.61	1.01	1.12
Pd	LA1	2.838	0.0227	3.60	0.73	1.68
Al	KA1	1.487	0.0053	0.68	0.54	1.68
Au	MA1	2.123	0.0136	2.95	0.32	1.68
Cl	KA1	2.622	0.0000	0.00	0.00	0.00
Na	KA1	1.041	0.0009	0.19	0.18	1.70
Total				**100.00**	**100.00**	**1.58**

Figure 28: Synthesis Run 4, Day 5 (EDX Elemental Analysis)

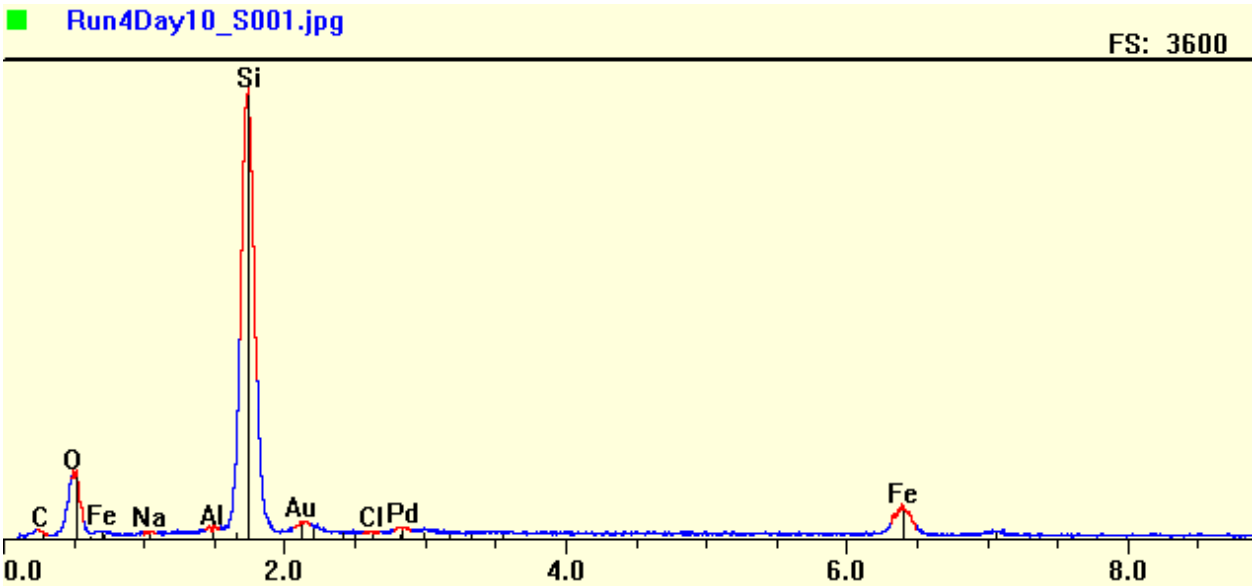

Figure 29: Synthesis Run 4, Day 10 (Global EDX)

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
Na	KA1	1.041	0.0000	0.00	0.00	0.00
C	KA1	0.277	0.0000	0.00	0.00	0.00
O	KA1	0.523	0.1790	54.25	70.89	34.06
Cl	KA1	2.622	0.0000	0.00	0.00	0.00
Si	KA1	1.740	0.2685	34.42	25.62	5.49
Al	KA1	1.487	0.0018	0.26	0.20	5.49
Fe	KA1	6.403	0.0602	7.19	2.69	1.01
Pd	LA1	2.838	0.0135	2.05	0.40	5.49
Au	MA1	2.123	0.0089	1.82	0.19	5.49
Total				**100.00**	**100.00**	**6.01**

Figure 30: Synthesis Run 4, Day 10 (EDX Elemental Analysis)

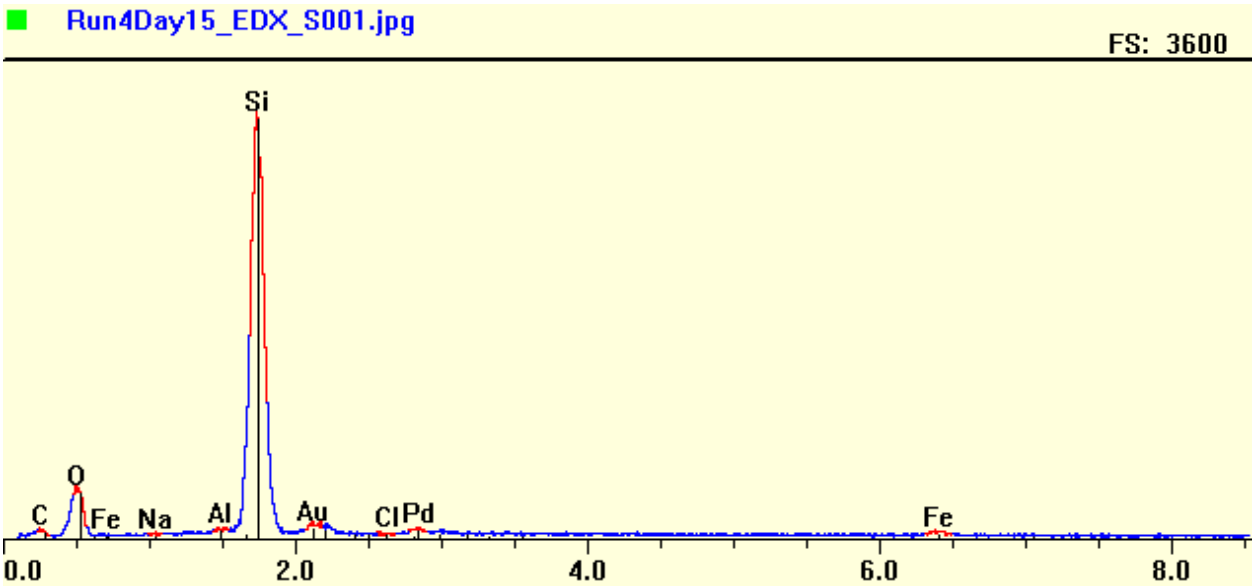

Figure 31: Synthesis Run 4, Day 15 (Global EDX)

Element	Line	keV	KRatio	Wt%	At%	ChiSquared
Na	KA1	1.041	0.0000	0.00	0.00	0.00
C	KA1	0.277	0.0000	0.00	0.00	0.00
O	KA1	0.523	0.1632	56.31	71.68	25.73
Cl	KA1	2.622	0.0000	0.00	0.00	0.00
Si	KA1	1.740	0.3100	37.13	26.93	3.66
Al	KA1	1.487	0.0020	0.26	0.20	3.66
Fe	KA1	6.403	0.0100	1.21	0.44	1.07
Pd	LA1	2.838	0.0171	2.69	0.52	3.66
Au	MA1	2.123	0.0112	2.39	0.25	3.66
Total				**100.00**	**100.00**	**4.25**

Figure 32: Synthesis Run 4, Day 15 (EDX Elemental Analysis)

Conclusions

Within this project, iron has been incorporated into ZSM-5 crystals. A synthesis has been developed in which iron is incorporated during the synthesis of zeolite crystals formed from silica gel beads. The most iron was incorporated into the crystalline structure after 10 days of the hydrothermal treatment at 170° C. Although 15 days of treatment yielded more zeolite crystals, there was less iron incorporated. More crystals were present in the samples which were synthesized with the solution containing more iron. No agitation was used in these syntheses, which resulted in the beads not being completely covered during synthesis. It is believed that a light agitation would correct this problem.

Recommendations

Although iron was successfully incorporated into ZSM-5 crystals during this study, the silica beads used in the synthesis remained largely unconverted. It is recommended that samples be pre-aged for 5 days prior to synthesis to allow adequate nucleation of crystals. A higher synthesis temperature may also be a viable investigation. Though many crystals formed on the surface of beads during the syntheses of this study, my of the beads had portions of the surface which were not covered with solution during synthesis. To remedy this, a gentle agitation should be performed during synthesis.

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Appendix 1: XRD Patterns

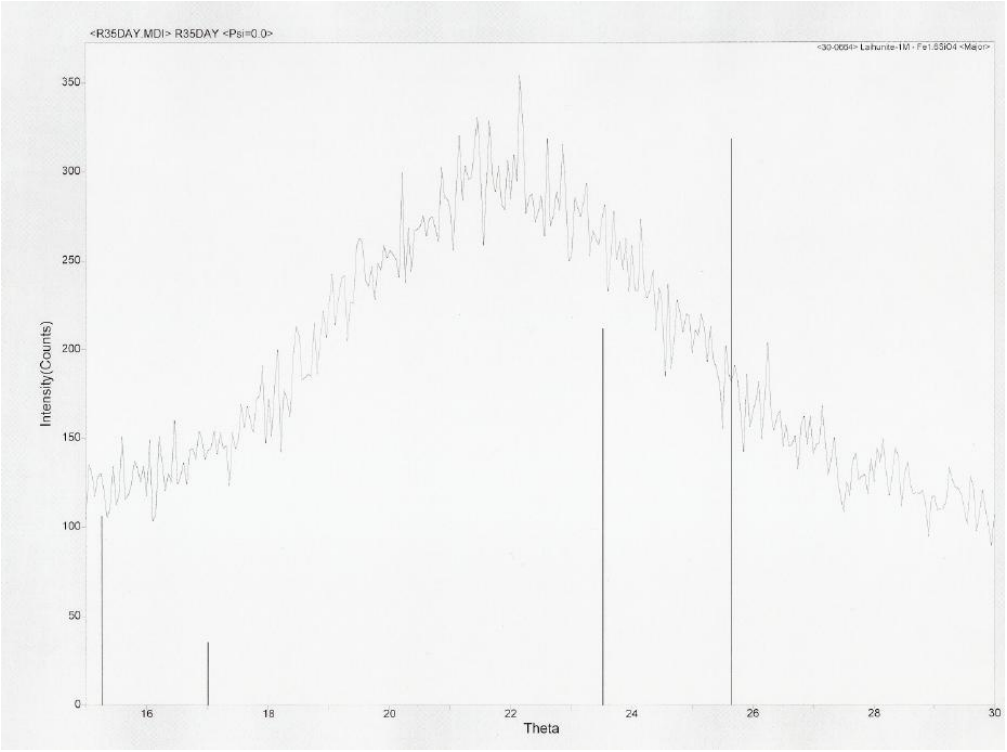

Figure 33: Run 3, Day 5 XRD (Laihunite – $Fe_{1.6}SiO_4$)

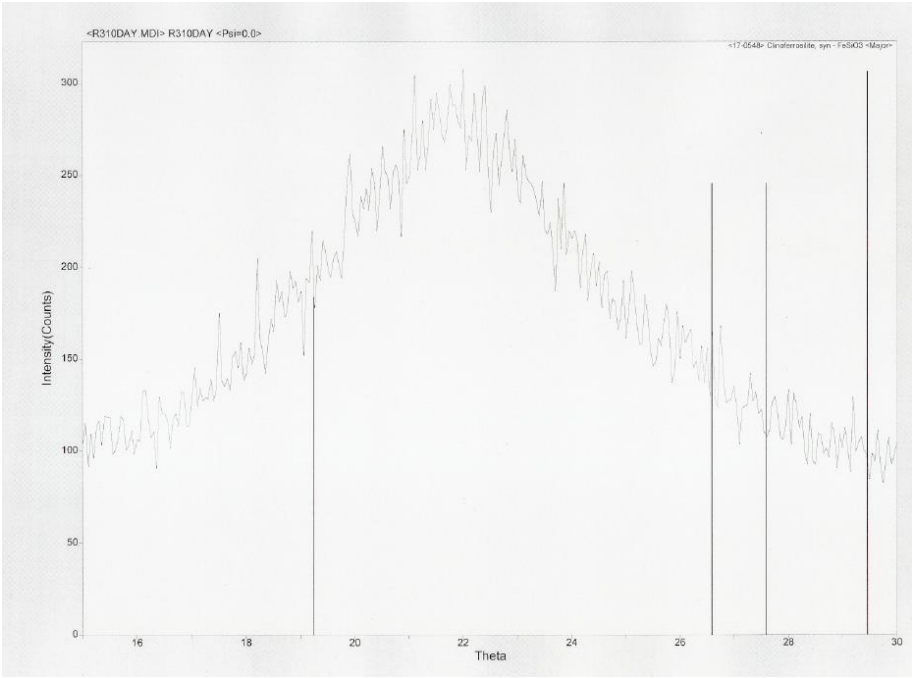

Figure 34: Run 3, Day 10 XRD (Clinoferrosilite – $FeSiO_3$)

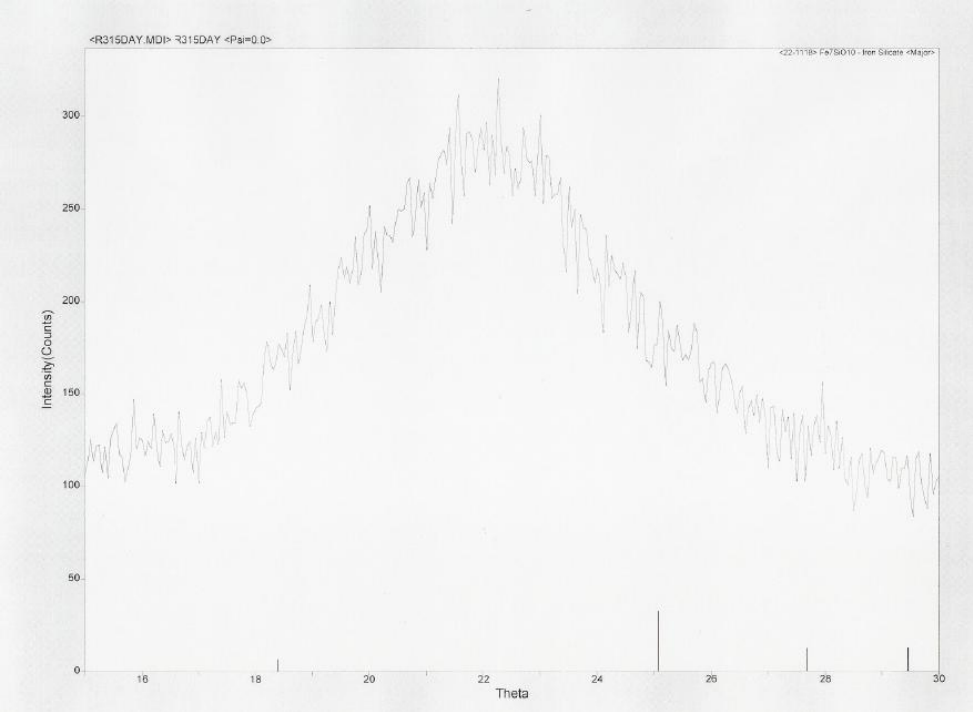

Figure 35: Run 3, Day 15 XRD (Iron Silicate – Fe_7SiO_{10})

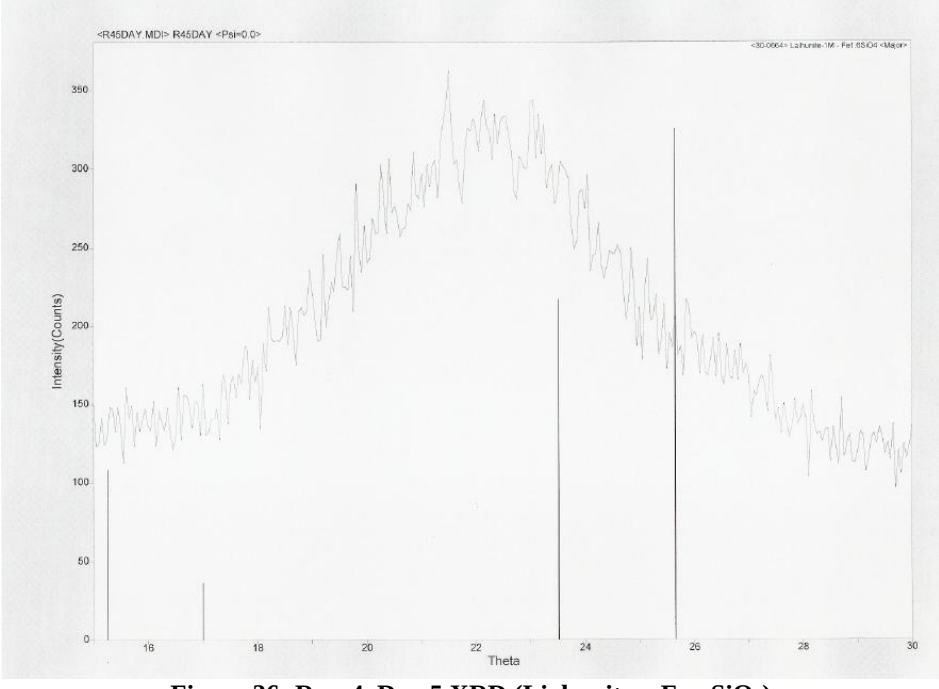

Figure 36: Run 4, Day 5 XRD (Liahunite – $Fe_{1.6}SiO_4$)

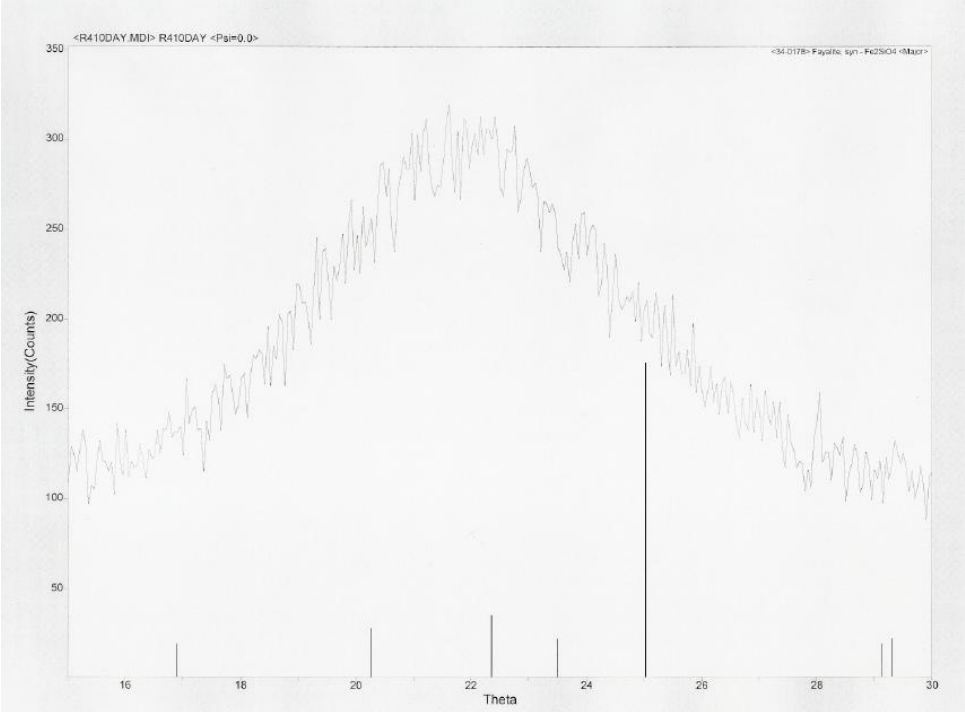

Figure 37: Run 4, Day 10 XRD (Fayalite – Fe_2SiO_4)

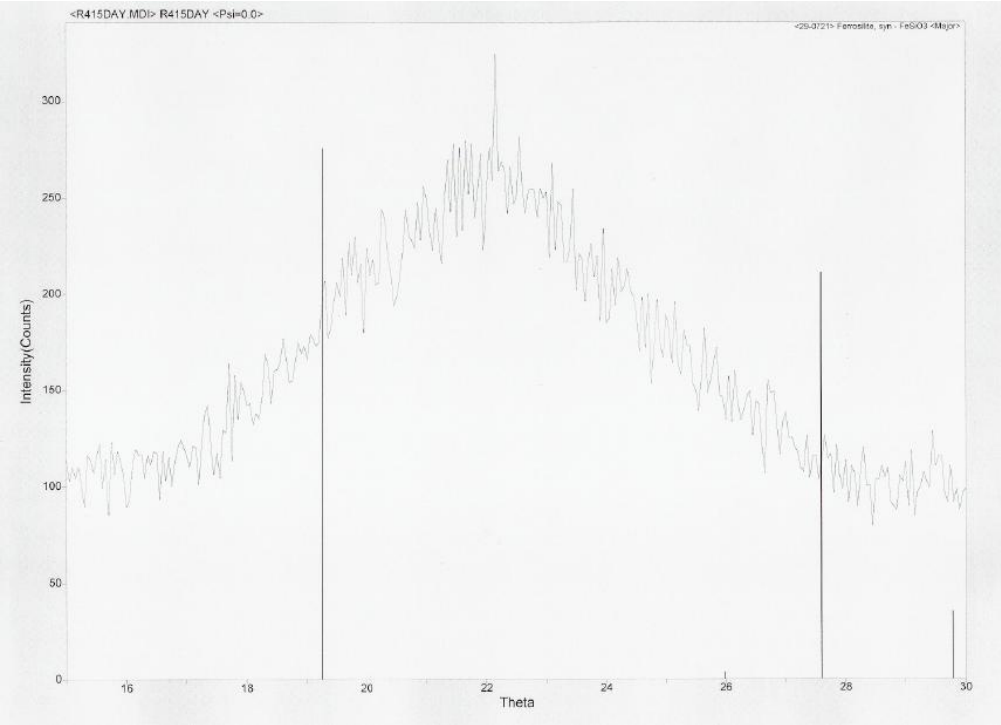

Figure 38: Dun 4, Day 15 XRD (Ferrosilite $FeSiO_{3)}$